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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Peter S. Christensen, et al.

Application No.: Not Yet Assigned

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Art Unit: N/A

For: PROCESS AND APPARATUS FOR THE  
PREPARATION OF SYNTHESIS GAS

Examiner: Not Yet Assigned

**CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS**

MS Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

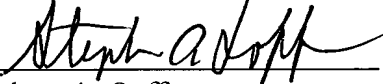
Applicant hereby claims priority under 35 U.S.C. 119 based on the following  
prior foreign application filed in the following foreign country on the date indicated:

<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2002 01431	September 26, 2002

In support of this claim, a certified copy of the said original foreign application is filed herewith.

Dated: September 24, 2003

Respectfully submitted,

By 

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# Kongeriget Danmark

Patent application No.: PA 2002 01431

Date of filing: 26 September 2002

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Title: Fremgangsmåde og apparat til fremstilling af syntesegas

IPC: C01B 3/38; B01J 8/06

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



**Patent- og Varemærkestyrelsen**  
Økonomi- og Erhvervsministeriet

13 August 2003

Åse Damm



**PATENT- OG VAREMÆRKESTYRELSEN**

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Process and Apparatus for the Preparation of Synthesis  
Gas

GB-283

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The present invention relates to a process and an apparatus for the preparation of synthesis gas. The preparation process includes catalytic steam and/or carbon dioxide reforming of a hydrocarbon feedstock. In particular, the invention provides an improved process of the above type including the steps of heated steam reforming of a hydrocarbon steam mixture in contact with a solid catalyst having activity in steam reforming and subsequently reforming the partially reformed effluent in a fired steam reformer.

Partial steam reforming upstream of a fired steam reformer in the form of pre-reforming of a hydrocarbon feedstock in the preparation of synthesis gas is well known in the art. Pre-reforming is generally employed with hydrocarbon feed containing higher hydrocarbons or for increasing the capacity of existing reformer plants. Process gas of the hydrocarbon feedstock and steam and/or  $\text{CO}_2$  is thereby introduced in a pre-reformer at temperatures of about  $450^\circ\text{C}$  to  $550^\circ\text{C}$ . By the steam reforming reactions proceeding in the pre-reformer, the temperature in the process gas usually decreases or increases slightly when carrying out the pre-reforming process depending on the hydrocarbon feedstock as it is an adiabatic operation.

In industrial synthesis gas preparation plants, the pre-reformed process gas to which  $\text{CO}_2$  may be added is subsequently reheated to the desired inlet temperature to the fired steam reformer by heat exchange with hot flue gas from the fired steam reformer. The usual inlet temperature into an industrial reformer is between  $600^\circ\text{C}$  and  $700^\circ\text{C}$ .

Introducing a flue gas heated steam reforming step in between the pre-reformer and the fired steam reformer will result in an increased utilisation of the flue gas heat content, while it is possible to keep the inlet temperature  
5 between 600°C and 700°C.

Increased utilisation of the heat content in the flue gas for reforming is desirable as it reduces the size of the fired reformer and reduces the waste heat used for steam  
10 generating thereby limiting the steam export, which may be undesirable.

Improved utilisation of heat in the hot flue gas from the fired steam reformer is disclosed in EP patent application  
15 No. 855,366. This publication describes a process whereby process gas to the steam reformer is partly reformed in a pre-heater coil provided with a thin film of steam reforming catalyst on the wall of the coil. A high amount of valuable heat in the flue gas is then transferred to and  
20 absorbed by the process gas through endothermic steam reforming reactions proceeding on the wall-coated catalyst. The coil dimension and amount of catalyst is thereby adjusted to increase the exit temperature in the partially reformed process gas from the catalysed pre-heater coil to  
25 the required temperature at inlet to the fired steam reformer.

The main disadvantage of this process is decreasing catalyst activity at long time operation of the catalysed pre-heater coil. This results in a coil exit temperature above  
30 the maximum allowable gas temperature at the inlet of the fired steam reformer. The increased coil exit temperature

is due to decreased heat absorption at diminished steam reforming in the gas. The catalyst has then to be reactivated or replaced with fresh catalyst on the coil wall. Replacement of catalyst in the pre-heater coil is a difficult and expensive operation when demounting the coil from the flue gas channel.

The objective disclosed in EP patent application No. 1,069,070 is to improve long term operability of a steam reforming process of the above type by compensating a decreasing catalyst activity in the catalysed pre-heater coil by means of an additional catalyst unit being easy to replace.

This publication discloses a process for the catalytic steam reforming of a hydrocarbon feedstock, and includes steam reforming a hydrocarbon steam mixture in contact with a first steam reforming catalyst being arranged in catalysed pre-heater coil in a flue gas channel from a fired steam reformer. Contacting partially reformed effluent from the catalysed pre-heater coil with a second steam reforming catalyst in a fired steam reformer follows this step. The process includes the further step of contacting the partially reformed effluent with an intermediate reforming unit arranged between the outlet of the catalysed pre-heater coil in the flue gas channel and the inlet of the fired steam reformer.

Loss of activity in the catalysed pre-heater coil unit during long time operation is compensated by steam reforming reactions in partially reformed effluent within the intermediate reforming unit. The intermediate unit is operated

at substantially adiabatic conditions and compensates decreasing steam reforming activity of the steam reforming catalyst (or catalysed hardware) in the catalysed pre-heater coil and the resulting temperature increase in the effluent from the catalysed pre-heater coil.

Besides providing the required temperature adjustment of the process gas below the maximum inlet temperature into the fired steam reformer at long term operation, a further advantage of the intermediate reformer unit is the siting of the unit outside the flue gas channel. To compensate decreasing activity in the catalysed pre-heater coil as described above, it will be necessary to replace or reactivate spent catalyst upstream the fired steam reformer. As mentioned earlier replacement of spent catalyst in a unit within the flue gas channel is time consuming and expensive to handle.

By arranging an intermediate catalyst unit outside the flue gas channel, spent catalyst is then replaced in the intermediate reformer unit and the replacement operation simplified considerably.

The processes described in EP 855,366 and EP 1,069,070 both have the disadvantage of difficult replacement of the catalyst in the catalysed pre-heater coil in the flue gas channel.

US patent No. 3,743,488 describes a process in which the hydrocarbon steam mixture is repeatedly heated in a flue gas stream and reacted in adiabatic reactors external to the flue gas stream, with steam reforming catalyst pellets.



This concept offers easier access for change of the catalyst in the external reactors. However, the use of many adiabatic reactor vessels is overall an expensive solution.

- 5 The process described in US patent No. 4,959,079 is designed with the purpose of improved utilisation of heat in the hot flue gas from the fired steam reformer. In the process the process gas to the steam reformer is partly re-
- 10 formed in a pre-heated section of the reformer tube that extends from the radiant chamber. Valuable heat in the flue gas is then transferred to and absorbed by the process gas through endothermic steam reforming reactions. However, heat exchange in counter current flow between the flue gas and the reforming tube is poor. Introducing fins on the re-
- 15 forming tube increases the heat transfer. Despite this the amount of heat transfer possible is relatively limited if the reformer tube length is to be kept at a reasonable length.
- 20 The process of the invention solves the problems occurring with the prior art by providing an improved process including the step of steam and/or CO<sub>2</sub> reforming of a hydrocarbon steam mixture in contact with a solid catalyst having activity in steam reforming. The solid catalyst is arranged
- 25 in piping system of a flue gas heated coil system, constituting a heated steam reforming unit. Subsequently, the effluent from the heated steam reforming unit is contacted with a steam reforming catalyst in a fired steam reformer. By locating the steam reforming catalyst of the heated
- 30 steam reforming unit as catalysed hardware in the piping system of the heated steam reforming unit, easy catalyst replacement is achieved, while at the same time achieving

improved utilisation of the heat content in the flue gas for steam reforming.

5 The invention therefore provides a process for the preparation of synthesis gas by catalytic steam and/or CO<sub>2</sub> reforming of a hydrocarbon feedstock comprising the following steps:

- 10 a. heating the reaction mixture of hydrocarbon and steam and/or CO<sub>2</sub> in a heated steam reforming unit integrated with the flue gas containing waste heat section from the fired tubular reformer in which reforming of the reaction mixture takes place by contact with a solid reforming catalyst
- 15 b. feeding the partially steam reformed mixture to the fired tubular reformer and further reforming the mixture to the desired composition and temperature, wherein the heated steam reforming unit is comprised of a piping system containing solid reforming catalyst being part of the process gas piping system integrated with the
- 20 flue gas-containing waste heat section.

The invention also concerns an apparatus for the preparation of synthesis gas according to the above process comprising the following:

- 25 a. an adiabatic pre-reformer for optional pre-reforming of a mixture of hydrocarbon and steam and/or CO<sub>2</sub>
- b. a fired tubular reformer with a flue gas-containing waste heat section for heating of a mixture of hydrocarbon and steam and/or CO<sub>2</sub> or of the pre-reformed
- 30 mixture
- c. a heated steam reforming unit

wherein the heated steam reforming unit is integrated with the flue gas-containing waste heat section from the fired tubular reformer, the heated steam reforming unit containing solid steam reforming catalyst.

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The various embodiments of the invention allow for easy replacement of the catalysed structured elements, efficient heat transfer between the flue gas and the process gas, and an economically attractive design due to the high level of integration of functions.

10

The application of the process of the invention is not limited to temperature intervals of 600°C-700°C.

15 The heated steam reforming unit is situated in the process gas piping system, and is integrated with the flue gas-containing waste heat section from the fired tubular reformer. The piping system can be structured in various ways. The heated sections can consist of several parallel  
20 tubes connected to common feed and product headers. For instance, the process gas enters a heating coil through an inlet header, followed by collection in an outlet header placed outside the heating section. This outlet header is connected to an inlet header for the next reheat coil section with a connecting element. The inlet and outlet headers and the transitional zone between the two headers form  
25 adiabatic zones.

30 In the inventive process solid catalyst e.g. catalyzed hardware such as structured elements that are catalysed with steam reforming catalyst can be placed in the any location in the heated zones and in the adiabatic zones.

In another embodiment of the invention, the first section of the heated steam reforming unit does not contain any catalyst and functions as a heating coil. The heated reaction mixture is subsequently transferred to a second section of the heated steam reforming unit containing catalyst designed to allow the process gas to reach to desired outlet gas temperature and composition. The catalyst may be located both in the adiabatic zones and in the heated zones of the second section of the heated steam reforming unit.

In a further embodiment of the invention, the heated steam reforming unit is comprised of several repetitions of sections without catalyst followed by sections with catalyst. This repetitive arrangement can commence either with a section without catalyst or by a section with catalyst. Likewise the last section can be either without catalyst or with catalyst.

The number of heating sections followed by reforming sections containing catalytic elements can be varied in the process of the invention.

In an other embodiment of the invention, in the heated steam reforming unit the catalyst is in the heated zones and is separated e.g. by spacers. This allows a larger degree of freedom in designing the system for a desired pressure drop and it de-couples the amount of catalyst used from the heat transfer area required.

Various solid reforming catalysts can be incorporated into the piping system of the heater. Catalysed hardware in the form of a structured element with a catalytic layer is

suitable for use in the process of the invention. Two types of structured elements are particularly suitable for the inventive process - the straight-channelled elements and the cross-corrugated elements.

5

The straight-channelled elements require adiabatic conditions and various geometries of these elements are possible. For example, straight channel monoliths are suitable for use in the process of the invention.

10

Cross-corrugated elements allow efficient heat transfer from the pipe wall to the gas stream. They are also suitable for use in the process of the invention especially in the heated zones.

15

Other catalysed structured elements can also be applied in the process of the invention. In addition other means of introducing catalyst activity into the system can be used in the process of the invention e.g. catalyst pellets, catalyst attached to the tube wall or catalyst attached to structures attached to the tube wall.

20

Any of the above catalyst types can be used in combination.

25

Fig.1 shows a conventional system with a pre-reformer having a reheating section and a reformer.

Fig. 2 shows a system representing an embodiment of the process of the invention.

30

Fig. 1 depicts a conventional system where process gas of hydrocarbon feedstock [1] and steam [2] is introduced in a

pre-reformer [20] at temperatures of about 450°C to 550°C. By the steam reforming reactions proceeding in the pre-reformer, the temperature in the process gas usually decreases or increases slightly when carrying out the pre-reforming process depending on the hydrocarbon feedstock, feedstock as it is an adiabatic operation. The pre-reformed product stream [4] and optionally carbon dioxide [8] enter the heating coil. The optional addition of CO<sub>2</sub> is indicated by a dashed line.

10

In industrial synthesis gas preparation plants, the pre-reformed process gas, to which CO<sub>2</sub> can be added, is subsequently reheated to the desired inlet temperature to the fired steam reformer [24] by heat exchange with hot flue gas [7] from the fired reformer [24]. The usual inlet temperature into an industrial reformer is between 500°C and 700°C.

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Fig. 2 illustrates an embodiment of the invention where the heated steam reforming unit is comprised of one heating section without catalyst [21] and one section with catalyst [23].

20

Hydrocarbon feed [1] is mixed with process steam [2] forming the feed stream [3] to the adiabatic pre-reformer [20]. This step is optional and can be left out if it is not required. CO<sub>2</sub> [8] can then be added if desired to the pre-reformed product stream [4] or in the case where pre-reforming is not required, to the hydrocarbon and steam feed stream [3]. The mixture then enters a heating section without catalyst of the heated steam reforming unit [21] integrated with the flue gas section [27] from a fired tu-

25

30

bular reformer [29] utilising the heat content of the flue gas [12] to heat the process stream. In heating section [21], the pre-reformed stream [4] is heated to, for example, 600°C-700°C before being collected in a header system [22]. Heated stream [4] is then fed to a heating section with catalyst of the heated steam reforming unit [23] integrated with the flue gas section [27]. Carbon dioxide may be added to the mixture if required at this point. Additional heat is transferred from the flue gas to the process gas and the heat is utilised to reform the hydrocarbon content of the process stream and forming stream [5].

In this embodiment the heated steam reforming unit comprises sections [21] and [23] and header system [22].

Several more heating sections and reaction sections can be included at this point. The number of heating sections and reaction sections depends on the desired effect e.g. gas composition or equilibrium gas temperature.

If desired CO<sub>2</sub> can be added to each section and/or header system of the heated steam reforming unit.

If no further heating sections and reaction sections are required, steam [5] is led to the reforming tubes [28] situated in the fired tubular reformer [29]. Here additional heat is added to the process by firing fuel, and the desired reformed product is collected from the reforming tubes.

A suitable structured element used in the embodiment described above is the cross corrugated element.

The advantages of the apparatus and the process of the invention are several. The most important advantage is that the solid reforming catalyst can easily be replaced because it is present in easily accessible tubes and is only present in the tubes in the places where it is required. In the process of the invention the amount of catalyst necessary for the process is completely decoupled from the necessary heat transfer area.

## 10     **Examples**

### **Example 1**

A comparison of the amount of catalyst required in a process of the invention as compared to a conventional process was made.

The conventional process was carried out by feeding hydrocarbon and steam into a pre-reformer followed by heating in a coil in the flue gas-containing waste heat section of a tubular reformer. Initially the feed was heated prior to passage through the first adiabatic reactor containing steam reforming catalyst pellets. Subsequently the mixture was reheated and reacted again, the number of reheating and reaction steps repeated until four reheating steps and four reaction steps altogether had been carried out.

In the a process of the invention a feed consisting of hydrocarbon and steam was fed into a pre-reformer followed by passage through a piping system constituting the heated steam reforming unit integrated with the flue gas-containing waste heat section of a tubular reformer. Initially the feed was heated prior to passage through the



first adiabatic header system containing a catalysed structured element and making up a reaction section. Subsequently the mixture was reheated and reacted again, the number of reheating and reaction steps repeated until four  
5 reheating steps and four reaction steps altogether had been carried out.

The initial inlet temperature to the first reheating coil after the pre-reformer was 450°C and the final outlet temperature was 650°C for both systems. Both systems were feed  
10 with a flow rate of 270 Nm<sup>3</sup>/h was led to the two steam reforming systems, and the product was withdrawn at a rate of 319 Nm<sup>3</sup>/h. The carbon flow rate was 100 Nm<sup>3</sup>/h. The space velocity of the conventional process was 10.000 - 15.000  
15 Nm<sup>3</sup> C<sub>1</sub>/hr m<sup>3</sup> catalyst. In the process of the invention the space velocity can be increased to 100.000 - 1.000.000 Nm<sup>3</sup> C<sub>1</sub>/hr m<sup>3</sup> catalyst because the catalyst is supported on a structured element.

20 The catalyst amount used in the process of the invention was 0.1-1.0 kg, while 6.7-10 kg was used in the conventional process.

The process of the invention allows the use of orders of  
25 magnitude less catalyst, allowing simplicity in design leading to superior economics.

#### Example 2

This example is based on the systems described in figures 1  
30 and 2, without CO<sub>2</sub> addition. A waste heat boiler was placed in the flue gas section of the reformer in order to obtain

overall high energy efficiency by recovering the heat content in the flue gas.

The figures shown in table 2 indicate that substantial savings are obtainable using the process of the invention.

Table 2

Comparison of the duty distribution in  
a Conventional process compared with  
process of the invention.

	Conventional	Invention
Primary reformer duty, Gcal/h	40.3	33.6
Reheat coil duty, Gcal/h	5.3	n.a.
Heated coil steam reformer unit duty, Gcal/h	n.a.	12.0
Total Reforming Duty, Gcal/h	45.6	45.6
Flue Gas Flow, Nm <sup>3</sup> /h	105166	92054
Waste heat boiler duty, Gcal/h	9.8	2.0

The results showed that the duty required by the reformer was much less in the case where the process of the invention was used. A smaller reformer can therefore be used in the process of the invention. The amount of steam generated was also reduced in addition to a flue gas flow rate reduction. Altogether substantial savings are achieved.

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## CLAIMS

1. Process for the preparation of synthesis gas by catalytic steam and/or CO<sub>2</sub> reforming of a hydrocarbon feedstock comprising the following steps:

a. heating the reaction mixture of hydrocarbon and steam and/or CO<sub>2</sub> in a heated steam reforming unit integrated with the flue gas containing waste heat section from the fired tubular reformer in which reforming of the reaction mixture takes place by contact with a solid reforming catalyst

b. feeding the partially steam reformed mixture to the fired tubular reformer and further reforming the mixture to the desired composition and temperature, wherein the heated steam reforming unit is comprised of a piping system containing solid reforming catalyst being part of the process gas piping system integrated with the flue gas-containing waste heat section.

2. Process according to claim 1 wherein the heated steam reforming unit is comprised of heating sections without catalyst and reaction sections containing solid reforming catalyst both being part of the process gas piping system integrated with the flue gas-containing waste heat section.

3. Process according to claim 2 wherein the reaction sections are comprised of both adiabatic zones and heated zones, where the solid steam reforming catalyst may be placed in any or all of these zones.

4. Process according to claim 1 - 3 wherein the reaction mixture of hydrocarbon and steam and/or CO<sub>2</sub> is pre-reformed prior to heating step a.
- 5 5. Process according to claims 1 - 4 wherein the solid reforming catalyst is a catalysed structured element.
6. Process according to claim 5 wherein the structured element is cross-corrugated.
- 10 7. Process according to claim 5 characterised in that the structured element is a monolith.
8. Process according to claim 5 wherein the structured element is a high surface structured element.
- 15 9. Process according to claim 1-4 wherein the solid catalyst is in the form of catalyst pellets.
- 20 10. Process according to claims 1-4 wherein the solid catalyst used is any combination of: catalysed structured elements, catalyst pellets, catalyst attached to the tube wall or catalyst attached to structures attached to the tube wall.

11. Apparatus for the preparation of synthesis gas according to claim 1 comprising the following:

a. an adiabatic pre-reformer for optional pre-reforming of a mixture of hydrocarbon and steam and/or CO<sub>2</sub>

5 b. a fired tubular reformer with a flue gas-containing waste heat section for heating of a mixture of hydrocarbon and steam and/or CO<sub>2</sub> or of the pre-reformed mixture

c. a heated steam reforming unit

10 wherein the heated steam reforming unit is integrated with the flue gas-containing waste heat section from the fired tubular reformer, the heated steam reforming unit containing solid steam reforming catalyst.

15 12. Apparatus according to claim 11 wherein the reaction sections with solid steam reforming catalyst in the heated steam reforming unit comprises adiabatic zones and heated zones where solid catalyst can be placed in the any location in the heated zones and in the adiabatic zones.

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**ABSTRACT**

5 Process and apparatus for the preparation of synthesis gas  
by catalytic steam and/or CO<sub>2</sub> reforming of a hydrocarbon  
feedstock comprising the following steps:

10 a. heating the reaction mixture of hydrocarbon and  
steam and/or CO<sub>2</sub> in a heated steam reforming unit in-  
tegrated with the flue gas containing waste heat sec-  
tion from the fired tubular reformer in which reform-  
ing of the reaction mixture takes place by contact  
with a solid reforming catalyst

15 b. feeding the partially steam reformed mixture to  
the fired tubular reformer and further reforming the  
mixture to the desired composition and temperature,  
wherein the heated steam reforming unit is comprised  
of a piping system containing solid reforming catalyst  
being part of the process gas piping system integrated  
with the flue gas-containing waste heat section.

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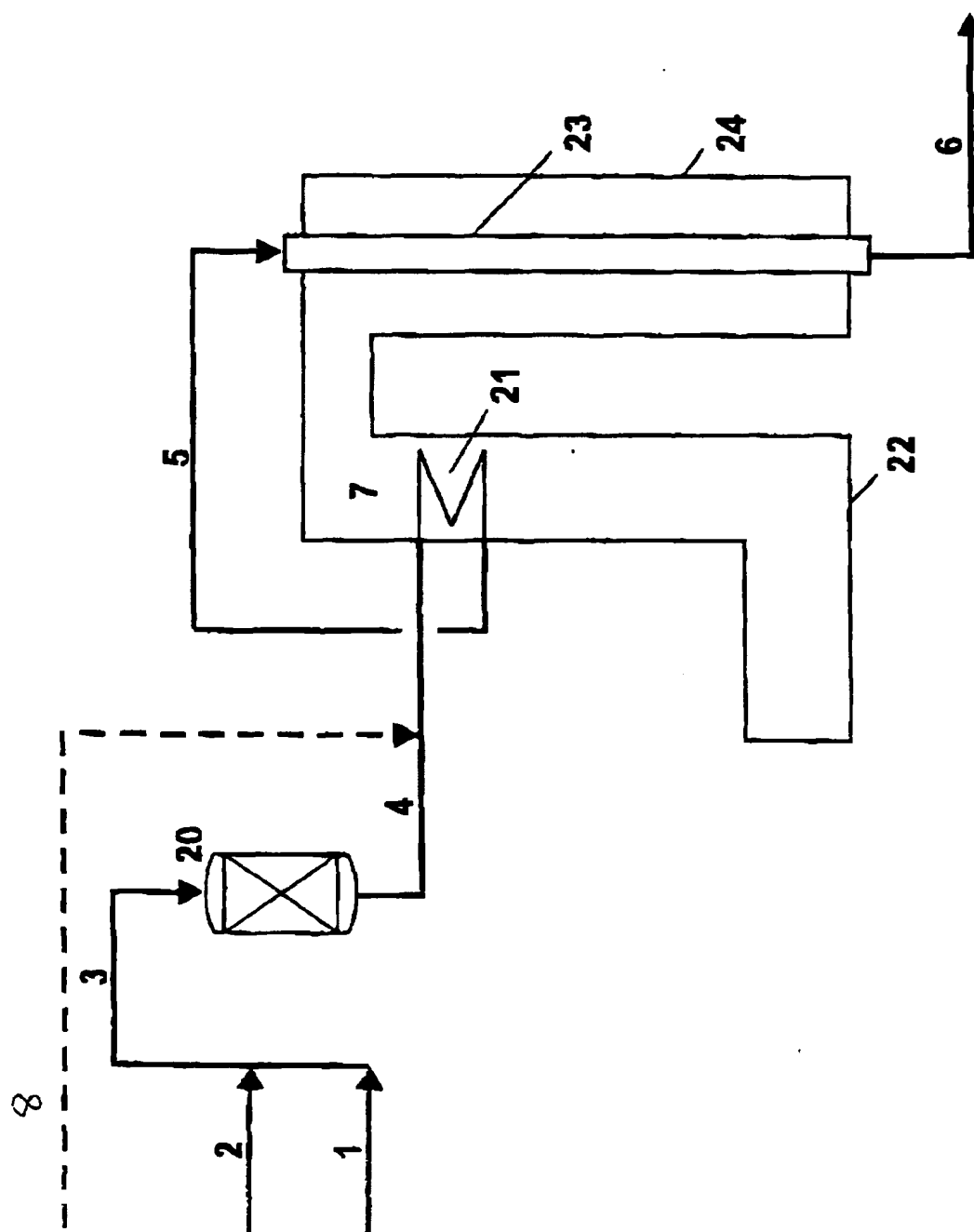


FIG. 1

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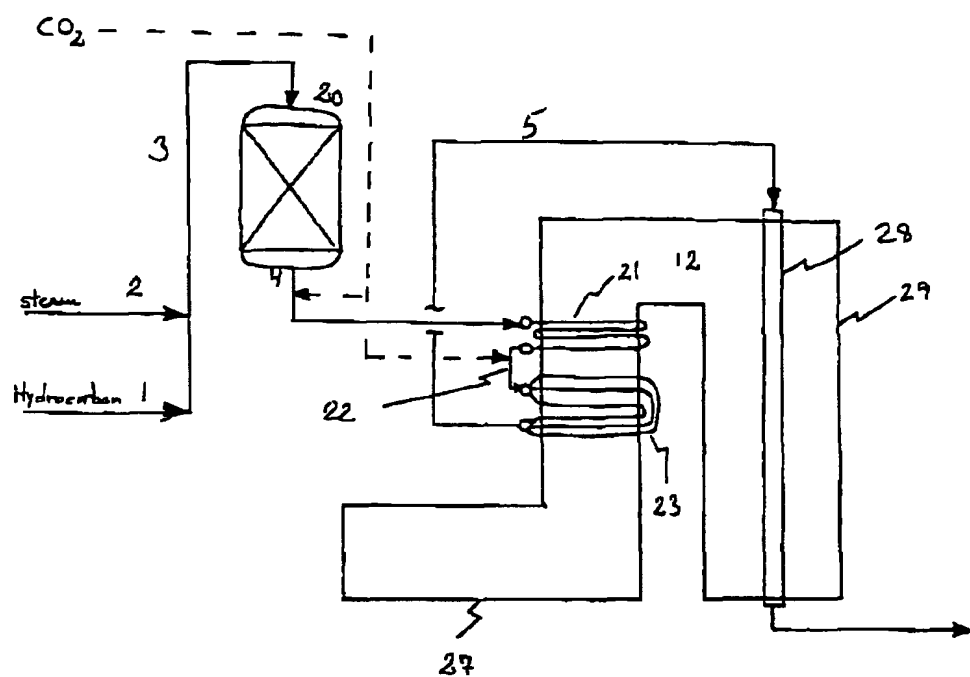


FIG. 2